

Synthesis, Characterization and Charge-Discharge Properties of Layer-Structure Lithium Zinc Borate, LiZnBO_3

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ABSTRACT

Layer-Structure lithium zinc borate, LiZnBO_3 , is prepared by a solid state reaction of $\text{LiOH}\cdot\text{H}_2\text{O}$, ZnO , and H_3BO_3 at 1000°C for 10 h. Highly preferred orientation and a layer-structure are observed in the powder XRD patterns and the SEM images, respectively. The Rietveld analysis indicates a monoclinic unit cell with space group $C2/c$, and the lattice parameters are refined as $a = 8.827 \text{ \AA}$, $b = 5.078 \text{ \AA}$, $c = 6.171 \text{ \AA}$, and $\beta = 118.86^\circ$. LiZnBO_3 shows the capacity of 17 mAh/g between 1.3 V and 4.3 V (vs. Li/Li^+) larger than ZnO .

Keywords: Oxide; Borate; Lithium; Zinc; X-Ray Diffraction; Battery

1. Introduction

Lithium metal phosphates (LiMPO_4), lithium metal silicates (Li_2MSiO_4) and lithium metal borates (LiMBO_3) have attracted considerable interest as cathode materials of lithium ion battery [1]. LiFePO_4 with olivine structure showed the reversible extraction and insertion of lithium at 3.5 V (vs. Li) [2], and this material has been already put to practical use by some lithium ion battery manufacturers. Analogs of LiFePO_4 have been explored extensively by many researchers, and the charge-discharge properties have been reported for lithium metal phosphates such as LiMnPO_4 , LiCoPO_4 [3-5], lithium metal silicates such as $\text{Li}_2\text{FeSiO}_4$ [6-9], and lithium metal borates such as LiMnBO_3 , LiFeBO_3 [10-15]. Polyanions with strong covalent bonds such as PO_4^{3-} , SiO_4^{4-} , BO_3^{3-} raise transition metal redox energies through inductive effect and stabilize the structure, thereby providing high performance and chemical safety.

LiZnBO_3 was first reported by Lehman and Shadow, and its preparation and characterization have been reported by a number of researchers [16-20]. In the ternary system of $\text{Li}_2\text{O}\text{-ZnO}\text{-B}_2\text{O}_3$, two polymorphs of LiZnBO_3 have been reported: one prepared by solid state reaction ($\alpha\text{-LiZnBO}_3$) and the other from hydrothermal synthesis

($\beta\text{-LiZnBO}_3$). Zinc-containing borates have been investigated aiming at the application to nonlinear optics and ferroelectrics, and the earlier reports describe the preparation of single crystals and structure analysis with a view to non-centrosymmetry. The crystal structure of $\alpha\text{-LiZnBO}_3$ is composed of ZnO_4 tetrahedra and BO_3 triangles by sharing O vertices and affords three-dimensional open channels that are occupied by lithium ions [20]. In spite of the attractive framework structure of LiZnBO_3 , there have been no reports on the lithium deinsertion/insertion properties of LiZnBO_3 . In this study, we successfully synthesized a layer-structure lithium zinc borate, $\alpha\text{-LiZnBO}_3$, by a conventional solid state reaction, and investigated its crystal structure, morphology, and lithium deinsertion/insertion properties.

2. Experimental

2.1. Synthesis

$\alpha\text{-LiZnBO}_3$ was synthesized from a stoichiometric mixture of lithium hydroxide, zinc oxide, and boric acid, *i.e.*, 2.10 g $\text{LiOH}\cdot\text{H}_2\text{O}$, 4.07 g ZnO , and 3.09 g H_3BO_3 . The mixture was placed in an alumina boat and heated in air at 1000°C for 10 h to yield a white powder product. In earlier reports, polycrystalline LiZnBO_3 has been ob-

tained by heating the stoichiometric mixture of ZnO and LiBO₂ at 1000°C for 12 h. After preliminary heating at 620°C for 1 h [19] or by heating the stoichiometric mixture of Li₂CO₃, ZnO, and H₃BO₃ for 750°C for 24 h [18], whereas single plate-like crystal of α -LiZnBO₃ has been obtained in a lithium borate matrix by heating the mixture of Li₂CO₃, ZnO, and H₃BO₃ with excess amount of Li₂B₄O₇ at 830°C [20]. In this study, LiOH·H₂O was used as the starting material instead of Li₂CO₃, and the heating temperature was set at 1000°C because the thermogravimetry and differential thermal analysis (DTA/TG, DTG-50, Shimadzu, Tokyo, Japan) of the starting mixture in air showed a broad exothermic peak above around 750°C.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were measured with a diffractometer (XD-D1, Shimadzu, Tokyo, Japan) using graphite-monochromatized Cu K α radiation at 30 kV and 20 mA. The crystalline parameters were refined by the Rietveld method using the RIETAN-2000 program [21]. Impurity peaks were excluded in the refinement. The morphology of α -LiZnBO₃ was observed by a scanning electron microscope (SEM, JSM-5610, JEOL, Tokyo, Japan). Each sample was ground with acetylene black and polytetrafluoroethylene (PTFE) binder into paste at a weight ratio of 84:4:12, and the paste mixture was pressed onto a nickel mesh for the lithium deinsertion/insertion measurements. The Ag/Ag⁺ electrode for non-aqueous solvent (RE-7, ALS Corporation Ltd., Tokyo, Japan) was used as a reference electrode, and natural graphite as a counter electrode. A 1 M LiClO₄ EC/DEC solution (EC:DEC = 1:1 in volume) was used as an electrolyte. The lithium deinsertion/insertion measurements were carried out in the galvanostatic mode in the range between $x = 0$ and $x = 0.5$, where x is the Li content per formula unit, *i.e.*, x in Li_{1- x} ZnBO₃. The electrochemical capacity of samples (mAh/g) was evaluated using the weight of the active materials.

3. Results and Discussion

White powder products were obtained by the solid state reaction at 1000°C for 10 h. The powder XRD pattern of the product and the structure refinement result are shown in **Figure 1**. The crystal structure was refined on the basis of monoclinic symmetry with space group $C2/c$ similarly to α -LiZnBO₃ in the earlier work [20], except for some impurity peaks. In the XRD measurements, the powder sample was solidified using glue to make each plane randomly oriented, because without the sample pretreatment with the glue the strongest (002) reflection was more than twenty times greater than the second strongest reflection due to the preferred orientation. This suggested that plate-like crystallites were formed by ani-

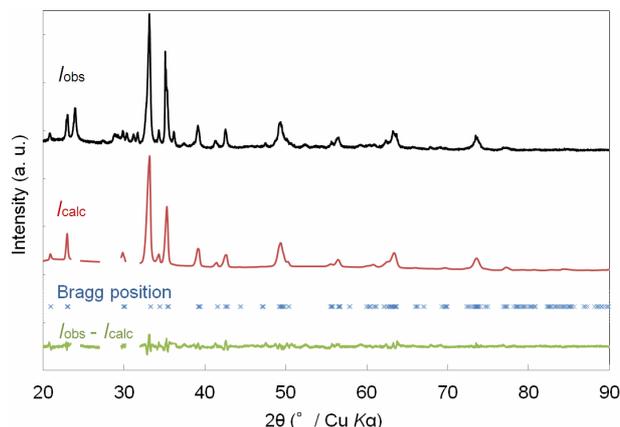


Figure 1. The observed XRD pattern (I_{obs}) of the LiZnBO₃ and the pattern refined by the Rietveld method (I_{calc}), along with the calculated Bragg position and the residual error ($I_{\text{obs}} - I_{\text{calc}}$).

sotropic crystal growth and the samples were prone to orient along the a-b plane. Structure parameters and selected interatomic distances are summarized in **Tables 1** and **2**, respectively, and view of the crystal structure of LiZnBO₃ is shown in **Figure 2**. The lattice parameters and monoclinic angle were calculated as $a = 8.827$ Å, $b = 5.078$ Å, $c = 6.171$ Å, and $\beta = 118.86^\circ$. In this structure, two ZnO₄ tetrahedra are linked together by edge-sharing (two O1 atoms) to form a Zn₂O₆ dimer, and the Zn₂O₆ dimer is linked to the six other Zn₂O₆ dimers by sharing oxygen vertices to form a three-dimensional framework. Boron atoms are located at the triangular void surrounded by three oxygen vertices to form BO₃ triangles. Lithium atoms are located in the three-dimensional channels surrounded by Zn₂O₆ dimers and BO₃ triangles. In this study the O₂ atom was located at 8f site with occupancy of 0.5, while it was located at 4e site (0, y , 1/4) with occupancy of 1.0 in the earlier work [20]. The two O₂ atoms with each occupancy of 0.5 were refined at extremely close two positions at the vertex of ZnO₄ tetrahedron, as shown in **Figure 2**, indicating the two possibilities of ZnO₄ tetrahedron shape. Such arbitrary property is probable in view of the occupancy of 0.5 for Zn1. In **Figure 3**, SEM images show secondary particles formed by aggregation of plate-like crystallites, and the crystallites are considered to be stacked perpendicular to the a-b plane. The present sample showed a lamellar structure consisting of plate-like crystallites stacked perpendicular to the a-b plane. This may be advantageous to lithium deinsertion/insertion because open channels in the crystallites are facing the electrolyte with large area. The conductivity of the powder compact of the present LiZnBO₃ estimated from the diameter of the semicircle in the cole-cole plot was 2.12×10^{-9} Scm⁻¹. It is much smaller than LiFeBO₃, 1.52×10^{-4} Scm⁻¹ [12], and as small as LiFePO₄, 2.2×10^{-9} Scm⁻¹ [23]. The low electric

Table 1. Structure parameters of LiZnBO₃ obtained by heating at 1000°C for 10 h. System: monoclinic. Space group: C2/c (No. 15), a = 8.827 Å, b = 5.078 Å, c = 6.171 Å, β = 118.86°, z = 4.

| Atom | Site | x | y | z | Occupancy |
|------|------|------------|-----------|------------|-----------|
| Li1 | 8f | 0.310 (4) | 0.603 (4) | 0.797 (4) | 0.50 |
| Zn1 | 8f | 0.3223 (7) | 0.567 (2) | 0.6965 (9) | 0.50 |
| B1 | 4e | 0.00 | 0.408 (4) | 0.25 | 1.0 |
| O1 | 8f | 0.167 (1) | 0.543 (4) | 0.295 (2) | 1.0 |
| O2 | 8f | 0.03 (2) | 0.172 (2) | 0.318 (2) | 0.50 |

Table 2. Selected interatomic distances (Å) of LiZnBO₃.

| Selected atom | Distance (Å) | Selected atom | Distance (Å) |
|---------------|--------------|---------------|--------------|
| Li1-O1 | 1.46 (4) | Li1-O1 | 1.93 (3) |
| Li1-O2 | 2.13 (3) | Li1-O2 | 2.31 (3) |
| Li1-O2 | 2.36 (3) | | |
| Zn1-O1 | 1.84 (1) | Zn1-O1 | 1.98 (2) |
| Zn1-O1 | 2.18 (1) | Zn1-O2 | 1.85 (2) |
| Zn1-O2 | 1.99 (2) | | |
| B1-O1 | 1.52 (1) | B1-O2 | 1.25 (9) |

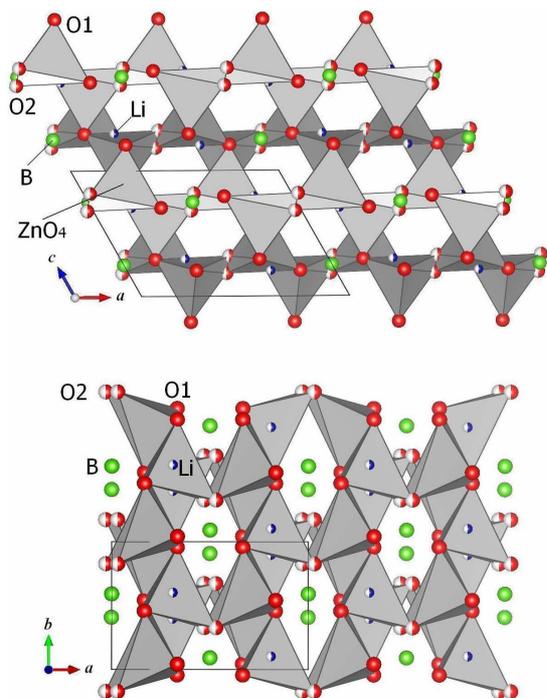


Figure 2. The crystal structure of the LiZnBO₃ projected along b-axis (upper) and c-axis (lower) visualized by VESTA3 [22]. Half-filled and fully-filled circles mean the occupancies of 0.50 and 1.0, respectively.

conductivity and/or lithium diffusivity suggests the necessity to give conductivity to LiZnBO₃ by treatment with carbon in order to improve the electrochemical

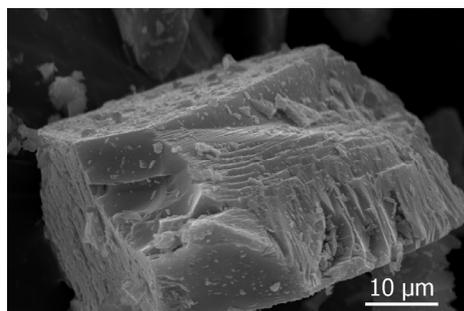


Figure 3. The SEM image of the layer-structure LiZnBO₃. The plane facing upward is the a-b plane.

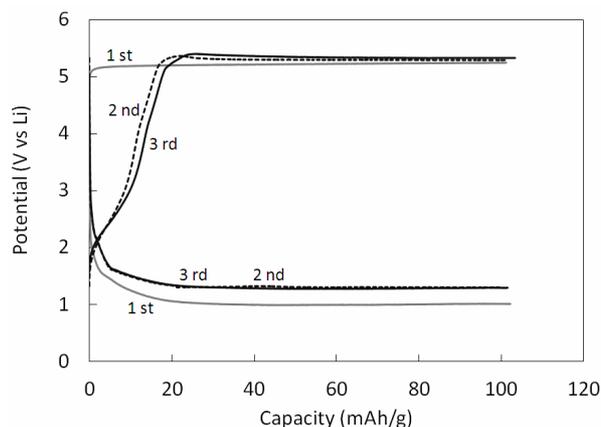


Figure 4. The charge-discharge curves of the LiZnBO₃ for first three cycles at rate of 20.3 mA/g.

performance.

Figure 4 shows the typical charge and discharge curves of LiZnBO₃ at charge/discharge rate of 20.3 mA/g. The first charge curve deviated from the second and third ones, indicating that the solid electrolyte interface (SEI) was formed at the cathode/electrolyte interface during the first charge process. The capacity between 1.3 V and 4.3 V (vs. Li/Li⁺) was 17 mAh/g, and the charge/discharge curves showed almost the same behavior for different charge/discharge rates from 2.03 mA/g to 203 mA/g. It should be noted that our comparative experiments using ZnO as an active material did not show such charge/discharge behavior. This is probably because LiZnBO₃ acted as an electric double layer capacitor (EDLC) and electric charge was accumulated at the interfacial region between the electrolyte and LiZnBO₃ powder. The layer structure of LiZnBO₃ was advantageous for EDLC over ZnO. The faradaic redox reaction of LiZnBO₃ was not observed as opposed to the cases of LiFeBO₃ and LiMnBO₃ [10-15], indicating that divalent zinc was not oxidized to trivalent zinc in LiZnBO₃ as well as in ZnO.

4. Conclusion

Lithium zinc borate, LiZnBO₃, prepared by the solid state reaction showed a layer-structure in the SEM images.

The XRD patterns well fitted to a monoclinic unit cell with space group $C2/c$, and the lattice parameters were refined as $a = 8.827 \text{ \AA}$, $b = 5.078 \text{ \AA}$, $c = 6.171 \text{ \AA}$, and $\beta = 118.86^\circ$. LiZnBO₃ showed the capacity of 17 mAh/g between 1.3 V and 4.3 V (vs. Li/Li⁺) larger than ZnO. The capacity was due to the EDLC between the electrolyte and LiZnBO₃ powder.

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